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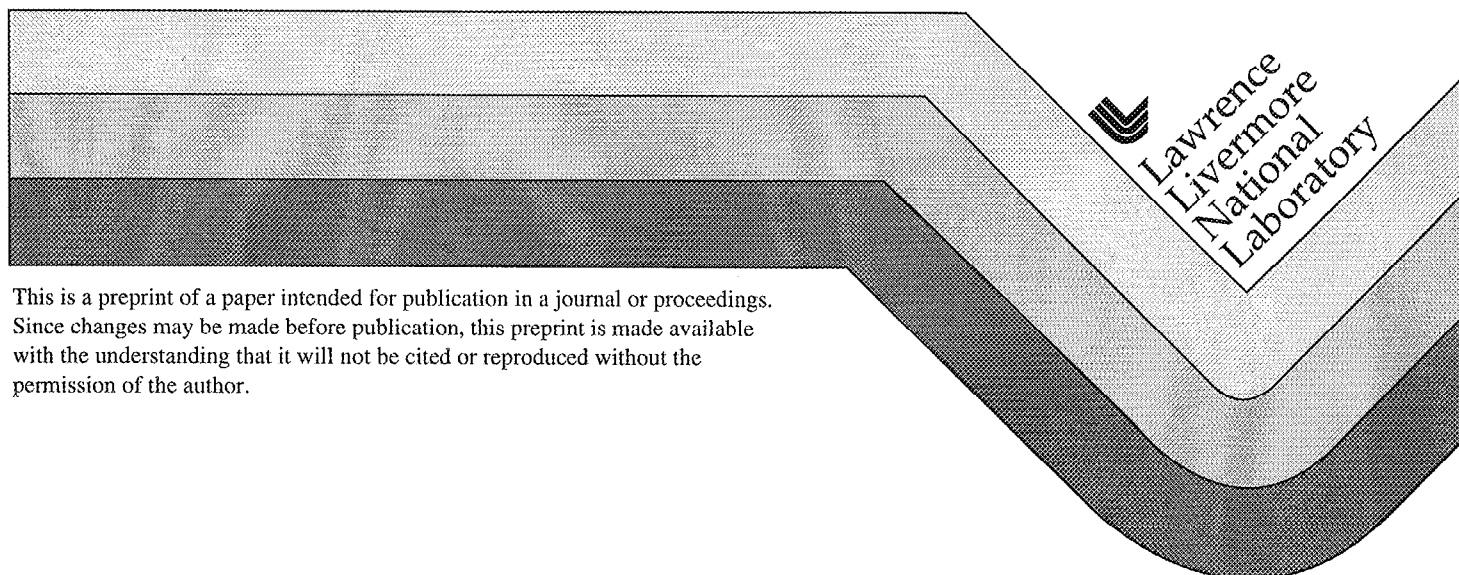
PREPRINT

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NATURAL BIODEGRADATION OF ORGANIC CONTAMINANTS IN GROUNDWATER

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ABSTRACT

There has recently been a growing awareness that natural processes are degrading contaminants of concern, and that the contribution these natural processes make to achieving cleanup goals needs to be formally considered during site-specific cleanup. Historical case data from a large number of releases has been used to evaluate the expectation for natural attenuation to contribute to the cleanup of petroleum hydrocarbons and chlorinated solvents. The use of historical case data has several advantages, among them: 1) sites can reduce characterization costs by sharing information on key hydrogeologic parameters controlling contaminant fate and transport, and 2) standard reference frameworks can be developed that individual sites can use as a basis of comparison regarding plume behavior.

Definition of cleanup times must take into account basic constraints imposed by natural laws governing the transport and natural degradation process of petroleum hydrocarbons. The actual time to reach groundwater cleanup goals is determined by these laws and the limitations on residual subsurface contamination attenuation rates, through either active or natural biological processes. These limitations will practically constrain the time to achieve low concentration cleanup goals. Recognition is needed that sites will need to be transitioned to remediation by natural processes at some point following implementation of active remediation options.

The results of an analysis of approximately 1800 California and 600 Texas fuel hydrocarbon (FHC) releases and 250 chlorinated volatile organic compound (CVOC) plumes will be summarized. Plume lengths and natural biodegradation potential were evaluated. For FHC releases, 90% of benzene groundwater plumes were less than 280 feet in length and evidence of natural biodegradation was found to be present at all sites studied in detail. For CVOC releases, source strength and groundwater flow velocity are dominant factors controlling groundwater plume lengths. After adjusting for these factors, biodegradation also appears to limit the length of CVOC plumes in many instances. The application of natural biodegradation processes as a remediation approach will depend on the time frame for anticipated beneficial use of the affected groundwater.

INTRODUCTION

The reduction of public health risk due to potential exposure of environmental contaminants is the prime reason for environmental restoration (ER) remedial actions. The cost of environmental restoration on a worldwide scale is potentially enormous. There is, therefore, a great need to 1) identify the types and levels of effort that are appropriate to reducing both the public health risk and the uncertainty of the risk, and 2) increase the benefit/cost ratio of the ER effort to prevent unnecessary expense.

A hypothetical cost versus cleanup model loosely based on the environmental cleanup experience at Lawrence Livermore National Laboratory (LLNL) is shown in figure 1. The model illustrated assumes a contaminant plume of CVOCs in groundwater that is remedied over the course of 50 years using pump and treat technologies. The overall effort for a single ER project can be divided into the following three phases: uncertainty reduction, engineering processes, and monitored natural attenuation. The major reduction in contaminant risk uncertainty occurs during the first few years prior to the start of cleanup. This is the period when site specific conceptual models are developed regarding the fate and transport of contaminants released at the site. The hypotheses regarding movement of contaminant plumes in groundwater and the potential for contaminants to naturally attenuate are developed as part of the conceptual model. Site specific characterization activities focus on confirming or denying these hypotheses. Typically, the cost of uncertainty reduction is small compared to the eventual costs of the engineered and monitored natural attenuation cleanup phases of remediation.

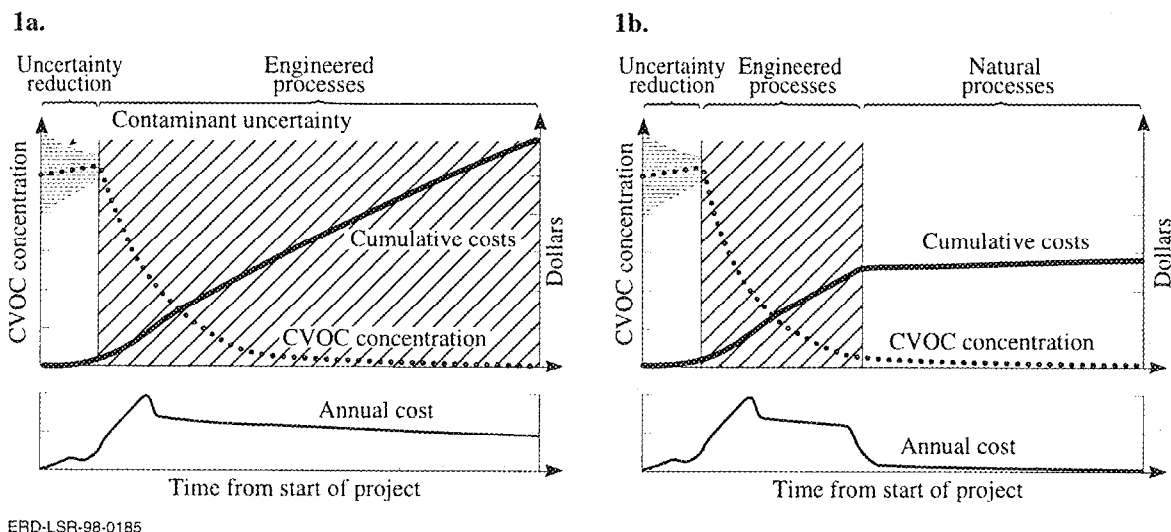


Figure 1. Hypothetical cost versus cleanup curves. 1a. Base case: total pumping time is 50 years; pumping stopped at 5 ppb. 1b. Alternative case: total pumping time 17 years; pumping stopped 200 ppb; natural processes used to complete cleanup.

The fastest cleanup likely occurs during the engineering processes phase and spans the 5-15 year period following the uncertainty reduction or characterization phase. It should be recognized that if natural attenuation processes are helping the cleanup, they too will be occurring during the engineered phase. Typically during pump and treat remediation, 50 percent of the total costs are spent to clean up the last few percent of contamination. Once the engineering processes phase has removed the major mass of contamination, the period of monitored natural attenuation or the utilization enhanced natural processes should begin. During this final phase of remediation, additional pumping to remove mass is not cost effective and natural processes, either biotic or abiotic, should be relied upon. During the implementation of pump and treat remedial alternatives, significant cost savings can be realized if engineering processes are stopped when they are no longer cost effective and natural processes are relied upon.

A basic assumption underlying a selection of a natural attenuation remedy, such as passive bioremediation, is that eventually background concentrations will be reached. A key question then is, "does this site have enough time to let nature take its course before receptors are impacted or the resource needs to be used?" Key decision making elements then become, 1) how fast is the natural process occurring and how do I measure this rate, 2) what can be done to take advantage of this

rate and what is the value of additional separate-phase hydrocarbon removal, and 3) what evidence is realistic and reasonable to reach a determination to apply natural attenuation?

CONCEPTUAL MODEL OF ORGANIC HYDROCARBON RELEASES

The idealized conceptual model of a dissolved organic hydrocarbon groundwater plume consists of two essential elements. The first element is the residual hydrocarbon material that provides mass to the dissolved hydrocarbon plume. The residual hydrocarbons can be characterized by light non-aqueous phase liquids (LNAPL) either as free product lenses floating on the capillary fringe, or as discrete ganglia entrapped within the vadose zone or even below the water table in the case of dense non-aqueous phase liquids (DNAPL). The second element is the dissolved plume extending downgradient of the residual hydrocarbon area which is affected by advective and dispersive transport, retardation, and passive biodegradation. Natural attenuation processes, particularly passive biodegradation, may limit the downgradient migration of the dissolved plume (Grbic-Galic and Vogel¹; Cozzarelli et al.²; Hess et al.³; Kazumi et al.⁴). The interplay of the two elements leads to the concept of a steady-state plume existing under dynamic equilibrium conditions, where the mass influx of dissolved contaminants from residual free product is balanced by mass loss via passive biodegradation, integrated across the spatial extent of the plume. As it expands from its initial inception, and as long as passive biodegradation processes remain active, this stabilization point will always be reached by advection and dispersion during the evolution of the plume.

The management of each of the processes associated with these two elements of the plume conceptual model will play different roles in the establishment and evaluation of site specific remedial goals and the application of natural process to reach these goals. These remedial goals may be functionally divided into two broad categories:

1. Control of risk to current existing downgradient receptors.
2. Reduction of contamination in the subsurface to some specified concentration within an acceptable interval of time to reduce uncertainties in the protection of future receptors.

The assessment of a site's dynamic equilibrium conceptual model, its integration into a site specific sources-pathways-receptors risk model, and the nature of the evidence available to assist in selection of a remediation process are all tightly coupled with the delineation of a site's remedial goals. It is often possible to assess the dynamic equilibrium model processes at a given site with the data at hand; risk to existing receptors is usually tied to the assessment of passive bioremediation to potentially limit plume movement (Remedial Goal No. 1). However, Remedial Goal No. 2 has eluded definitive analyses because the necessary data are often not available to predict residual hydrocarbon depletion rates (and will likely not be available for the large majority of private/commercial organic hydrocarbon release sites). The reasons behind this reflect the nature of the evidence concerning passive bioremediation processes and residual hydrocarbon attenuation rates (by natural and/or engineered means), respectively.

ROLE OF HISTORICAL CASE ANALYSIS IN THE APPLICATION OF MONITORED NATURAL ATTENUATION

Historical Case Analysis can be used to predict how contaminant plumes may behave in various hydrogeologic settings, which remedial goals are appropriate, and when monitored natural attenuation is a useful remedial approach. Remedial investigations conducted on organic hydrocarbon plumes usually strive to identify site-specific features of the local hydrogeology and the distribution of contaminants. This information is needed to facilitate development of appropriate cleanup strategies. As such, broad trends in relationships between plume behavior and key site variables across a number of sites are not usually analyzed in any systematic and quantitative way. Historical case analyses offer a means to address this shortcoming in our

knowledge of contaminant hydrology. The approach of these studies was to collect hydrogeologic and organic hydrocarbon plume data from a large number of sites representing diverse environmental settings and release scenarios and statistically compare plume behavior to mean site variables such as groundwater velocity or biotransformation potential. In this way, the relative effects of different key variables on plume behavior can be compared with one another under actual field conditions. Such information is potentially useful in providing guidance for developing site specific conceptual model hypotheses, planning remedial investigations, targeting cleanup priorities, and selecting appropriate remedial alternatives. Moreover, by creating a database of plume behavior and hydrogeologic variables, a reference frame is established within which individual plumes may be compared to other plumes in similar settings. This affords the opportunity to identify plumes that behave unusually compared to a majority of the plumes in similar settings. This will help identify unusually short plumes that are likely candidates for a monitored natural attenuation remedial approach or unusually long plumes that warrant further examination.

The findings and conclusions resulting from three historical case analysis (HCA) studies can be used to illustrate this approach. Two HCA studies examined the behavior of petroleum hydrocarbon plumes in California and Texas, United States of America (USA). The third study examined USA historical case data, nationwide, on groundwater contamination by chlorinated volatile organic compounds (CVOCs). The purpose of these studies was to evaluate the hydrogeologic factors affecting the extent and growth behavior of organic hydrocarbon plumes in groundwater from a statistical perspective involving data from multiple sites. This evaluation is important because of the significant role that plume behavior plays in the management of human health, environmental decision making, and resource risk evaluation.

RESULTS FROM TWO LEAKING UNDERGROUND FUEL TANK STUDIES

In July 1994, the California State Water Resources Control Board (SWRCB) Underground Storage Tank (UST) Program embarked on an evaluation of the Leaking Underground Fuel Tank (LUFT) cleanup procedures. To support this effort, the SWRCB UST Program contracted with the Lawrence Livermore National Laboratory (LLNL) and the University of California at Berkeley, Davis, Los Angeles, and Santa Barbara to form a team of scientific experts (the LLNL/UC LUFT Team) to evaluate historical impacts of LUFTs to California's groundwater (Rice et al.⁵), review the existing LUFT cleanup decision-making process, and submit recommendations for improvement (Rice et al.⁶). Following this study, a similar approach was taken by the Texas Bureau of Economic Geology (Mace et al.⁷). Table 1 summarizes the findings of these two studies. Benzene plumes were found to be limited in length to no more than about 380 feet in 90% of the 488 combined cases evaluated. Both studies also evaluated whether plumes were growing, stable, or declining in length and average concentration. These results are summarized in Table 2. A majority of the plumes were found to be either stable or declining in length and concentration.

These studies concluded that with rare exceptions, petroleum fuel releases will naturally degrade (passively bioremediate) in California's and Texas's subsurface environments, typically without regard to hydrogeologic setting. Passive bioremediation can control groundwater contamination in two distinct ways. First, passive bioremediation substantially lowers the risk posed to down-gradient risk receptors through plume stabilization. Second, passive bioremediation actively destroys fuel hydrocarbon mass in the subsurface, leading to remediation of contamination over time (e.g. eventual decline and depletion of the dissolved hydrocarbon plume). From a risk management viewpoint, the stabilization of the dissolved plume is the most important contribution of passive bioremediation. These studies recognized that "long plumes" exist, but these are rare, and fuel hydrocarbon release sites with relatively short, stable, or decreasing plumes should not be treated in the same manner as sites with long, growing plumes.

Table 1. Summary of California and Texas historical case analysis of benzene plume lengths associated with petroleum hydrocarbon releases. Plume lengths are measured to the 10 part per billion isoconcentration contour.

	90% quantile	99% quantile
California ^a average site 10 ppb benzene plume length, ft.	306	915
Texas ^b average site 10 ppb benzene plume length, ft.	380	1,200
Total number of sites evaluated	271	217 ^c

^a Rice et al.⁵

^b Mace et al.⁷

Table 2. Summary of California and Texas historical case analysis indicating changes in average benzene plume concentration with time.

	Percent of total number of sites	
	California ^a	Texas ^b
Decreasing benzene concentrations	59%	58%
Increasing benzene concentrations	8%	14%
Stable benzene plumes	33%	27%
Total number of sites evaluated	271	217 ^c

^a Rice et al.⁵

^b Mace et al.⁷

^c Status of 1% of the Texas sites could not be evaluated.

The use of passive bioremediation still requires site characterization and an assessment of potential risks and the need for active source removal must be addressed on a site-by-site basis. Source removal includes removing leaking tanks and lines, and removing free product and petroleum fuel saturated soil, as much as economically and technically feasible. Although active source removal will contribute to higher rates of contaminant remediation in some instances, it will not diminish the risk posed to down-gradient risk receptors by a plume which has already stabilized as a result of passive biodegradation.

U.S. DEPARTMENT OF DEFENSE PETROLEUM CLEANUP DEMONSTRATION SITES

The California LUFT HCA Study recommended that a series of LUFT sites be identified where the application of natural attenuation cleanup approaches could be demonstrated. As a result, ten Department of Defense (DoD) sites were selected to participate in a DoD Petroleum Hydrocarbon Cleanup Demonstration (PHCD) Program. This program will be referred to as the DoD LUFT Cleanup Demonstration Program. Sites were selected to represent each branch of the military services with bases in California, and as many of the California Regional Water Quality Control

Boards (RWQCBs) and diverse hydrogeologic settings in California where fuel hydrocarbon (FHC) contaminant cleanup problems occur as possible.

The DoD LUFT Cleanup Demonstration Program concluded that the role of passive bioremediation in controlling the behavior of dissolved hydrocarbon plumes may be evaluated through both primary and secondary field evidence. Primary evidence includes quantitative evaluation of plume stability or plume shrinkage based upon trends in historical groundwater data. Although primary evidence of plume stability or decline provides the strongest arguments to support a passive bioremediation hypothesis at a given site, such evidence may not be available because adequate historical groundwater monitoring may not exist. This has been the case with most of the DoD sites included in the Demonstration Program. In these instances, short-term monitoring data providing secondary lines of evidence, in conjunction with modeling where appropriate, may support a hypothesis for the occurrence of passive bioremediation. Consequently, means for assessing the role of passive bioremediation through secondary lines of evidence were addressed.

Secondary evidence includes indirect indicators of passive bioremediation, such as variations in key geochemical parameters between measurements in fuel hydrocarbon-impacted areas and background. These include concentrations of electron acceptors (O_2 , NO_3^- , SO_4^{2-}), reduced redox reaction by-products (Fe^{2+} , Mn^{2+} , CH_4), as well as bicarbonate alkalinity, pH, and redox potential (E_h) (Chappelle⁸; Borden et al.⁹; Vroblesky et al.¹⁰). However, background variability in a number of these parameters complicates the task of data interpretation, particularly in the case of small data sets. Correlation analyses and population means testing have been applied to geochemical indicator data at several of the Demonstration sites to identify which parameters are the most reliable indicators. The results of the analyses suggest that the most direct indicators of the local redox environment – Fe^{2+} , Mn^{2+} , CH_4 , E_h – yield the most consistent evidence of hydrocarbon biodegradation. Indicators which rely largely on mass balance – O_2 , NO_3^- , SO_4^{2-} , bicarbonate alkalinity – may be less robust. These findings, presented in detail in (McNab¹¹), may provide guidance in both the collection and interpretation of groundwater monitoring data at hydrocarbon contamination sites in general.

The estimation of representative passive bioremediation rates of dissolved hydrocarbon plumes at a site, particularly in the absence of adequate historical monitoring data, is not a straightforward issue. One method involves exponential regression of measured concentrations as a function of distance downgradient from the source area along the longitudinal axis of the plume (Buscheck and Alcantar¹²). This approach assumes one-dimensional solute transport model which accounts for the presence of a continuous boundary concentration and a uniform first-order degradation coefficient. It must be recognized that this type of analysis is easily subject to misinterpretation, particularly when few monitoring points are used. This is because the dispersive nature of solute transport can produce concentration profiles which closely resemble those associated with a degrading contaminant even in the absence of any transformation processes.

Another important lesson learned from the DoD LUFT Cleanup Demonstration Program was that key to the appropriate use of natural attenuation is the uncertainty associated with how long cleanup using this approach will take. The term "complete cleanup" means that no residual hazards are associated with the site, and the site can be used without restriction. Several issues are associated with determining "how clean is clean enough." One issue is the time frame for anticipated beneficial use of the site; another is the technical feasibility of removing all traces of FHCs at a site. Eventually, all of the more volatile and soluble FHCs, even methyl *tertiary*- butyl ether (MTBE), will be degraded or attenuated to below detection limit concentrations, even without active remediation. In some cases this process will occur over several decades; perhaps as long as a century.

Decades is a tolerable period of time for natural degradation processes to operate if the FHCs are (1) relatively immobile in the subsurface soil at a depth where human or ecological exposure is highly unlikely, or (2) have impacted groundwater where beneficial use is not probable. Risk

based site evaluations can be used to identify low risk sites where the time required for passive bioremediation to complete the cleanup of residual FHC is allowable. In some cases, free product removal may not be needed from a risk point of view based on current land use, but that some free product removal effort may be required to reduce the uncertainty associated with clean up time estimates and to improve long term risk management.

On the other hand, fifty years may be perceived to be a long time to most regulators and to the public. Institutional planning cannot be expected to be accurate 50 years into the future. Rather than engage in long term active remediation, the "reasonableness" of a cleanup period may be extended by placing more resources on strengthening institutional processes or controls that reduce the uncertainty associated with future risk.

The evaluation of natural depletion of residual hydrocarbons requires estimates of light non-aqueous phase liquid (LNAPL) dissolution rates into groundwater as well as volatilization rates into the vadose zone. For engineered residual hydrocarbon removal, this requires an estimate of mass removal rates as a function of time. In any event, an accurate estimate of residual LNAPL volume is also necessary. From a characterization viewpoint, much of this additional information is extremely difficult to obtain or to estimate accurately. As a result, the time scale required for plume collapse, by natural source weathering and/or engineered source removal, often cannot be predicted with high confidence.

If the residual hydrocarbon attenuation rate holds the key to plume remediation within a "reasonable" time frame, then there is an obvious inclination to attempt to remove residual hydrocarbon product to accelerate the cleanup process beyond the rate provided by natural mechanisms (dissolution and volatilization, combined with passive bioremediation). Most environmental regulators in the USA require active remediation of residual free product to demonstrate that it is technically or economically unfeasible to achieve site specific cleanup levels. Fate and transport models can be used to compliment the evaluation, but a purely analytical evaluation in support of an unfeasibility determination appears to be unacceptable to many of the regulators.

Typical residual hydrocarbon removal technologies at LUFT sites include free-product removal, soil vapor extraction, bioventing, and over-excavation. Several factors should be considered in the selection of residual hydrocarbon zone treatment technologies:

- If the remedial goal is only to ensure plume stabilization, and passive bioremediation is shown to be effectively limiting plume migration, then treatment of the residual hydrocarbon zone soils is irrelevant.
- If the remedial goal is one of plume mitigation within a decade, then active residual hydrocarbon zone treatment will likely be required.
- Each active remedial technology has a practical limitation of effectiveness and so technologies must often be applied in a sequence, with passive bioremediation being the final step in the treatment train.
- The benefits of LNAPL removal via over-excavation were illustrated by the results of the historical analysis of California leaking underground fuel tank (LUFT) cases (Rice et al.⁵). These results indicated that over-excavation of the residual hydrocarbon area at LUFT sites with shallow groundwater increased the probability of observing both low average benzene plume concentrations and a decrease in benzene plume concentrations with time.
- Conventional LNAPL free product extraction has limited effectiveness beyond about 30% to 50% of the original product mass. Conventional skimming may recover as much as 30%, high vacuum as much as 50%, and steam flooding as much as 90% of the original product mass (Beckett and Lundegard¹³).
- LNAPL recovery efforts are especially difficult in cases characterized by low free product thickness or relatively fine-grained soils.

- LNAPL extraction efforts are self-limiting in effectiveness. Recovery decreases with time because the removal of the most mobile portion of the LNAPL phase reduces the mobility of the remaining material. This occurs when capillary forces exceed the driving forces associated with the LNAPL gradient.
- Decision-makers should carefully weigh the benefits and costs of active remediation, and should recognize that active remediation systems by themselves rarely achieve drinking water standards in short time frames at groundwater-impacted sites.
- The main benefit of active remediation at most LUFT sites is not a reduction in risk of adverse impacts (because the maximum impact has usually occurred before it is observed), but is instead a reduction in time frame over which restoration of the site occurs.

The DoD LUFT Cleanup Demonstration Program also concluded that no reasonable amount of active remediation will be able to remediate long-chain molecules to non-detect levels. From a fate and transport perspective, these long-chain molecules are not as likely to advect or diffuse and, therefore, do not represent a "dynamic" risk. They may represent a "static" risk, whereby if an individual drilling or digging through them, may be exposed. Their exposure will be limited, however, due to the relatively low taste and odor thresholds associated with FHCs (which represent an "upper boundary" to the potential risk).

The DoD LUFT Cleanup Demonstration Program resulted in four recommendations: 1) consistent guidance should be developed to define target time frames for achieving remedial goals, 2) local groundwater use and distribution agencies should have greater involvement in the establishment of reasonable time frames for anticipated beneficial use, 3) guidance is needed that formally recognizes that achieving low $\mu\text{g/L}$ concentrations is not practicable in the short term (<10 years) at most sites with groundwater impacted by fuel hydrocarbons, and 4) better approaches are needed for estimating residual petroleum hydrocarbons longevity.

CHLORINATED VOLATILE ORGANIC COMPOUND HISTORICAL CASE ANALYSIS STUDY

There are several US national initiatives that continue to re-evaluate CVOC cleanup processes. These include efforts by the United States Environmental Protection Agency (US EPA) to reconsider the manner in which CVOC toxicity factors are developed, efforts by many investigators to evaluate the mechanisms and impacts of natural attenuation at individual sites, and efforts by the Department of Energy (DOE), the Department of Defense (DoD), and the US EPA to evaluate the use of enhanced natural attenuation during CVOC cleanup and to demonstrate new remediation technologies. Missing from these initiatives is a cross cutting evaluation of the large amount of CVOC historical case data that is available.

A recent CVOC historical case study (McNab et al.¹⁴) involved the collection and analysis of data from 65 sites representing a variety of hydrogeologic settings and release scenarios (e.g., large industrial facilities, dry cleaners, landfills). Data collection involved a variety of federal and state agencies and included participation from the U.S. Department of Defense, the Department of Energy, and private industry.

Plumes were defined per CVOC per site, yielding a total of 247 plumes delineated by the 10-ppb contour and a subset of 134 plumes delineated by the 100-ppb contour. A total of 16 CVOCs were included in the study. The mean rate of plume growth among the CVOC plume population in the database was estimated by two different methods. One method relied upon estimates of plume length as a function of time at sites with sufficient time series data. The second method utilized the apparent relationship between maximum plume length and the inferred plume age based on site history. In both cases, the mean rates of plume growth (20 ft/yr. and 46 ft/yr., respectively) appear reasonably consistent with the mean groundwater velocity in the site database (76 ft/yr.).

With regard to specific relationships, the CVOC Historical Case Analysis Study found:

- Plume length is somewhat correlated with the maximum historical concentration (as a surrogate variable for source area mass) on a per contaminant, per site basis. The correlation is more pronounced in plumes defined by the 100-ppb contour than those defined by the 10-ppb contour. This difference is consistent with expectation given the closer proximity of the 100-ppb contour to the source area.
- Maximum plume length per site is somewhat correlated with estimated mean site groundwater velocity, or alternatively mean site hydraulic conductivity. In this case, maximum site plume length was treated as the dependent variable since the longest plume at any given site would presumably reflect the influence of mean groundwater velocity to a greater degree than very short plumes that may be limited by other factors such as source mass. The correlation appears to be stronger for 10-ppb-defined plumes than 100-ppb-defined plumes, the 100-ppb contour perhaps being influenced to a greater extent by other variables (e.g., source mass or contaminant transformations).
- A categorization scheme for classifying sites for evidence of reductive dehalogenation has been developed based upon the presence or absence of suspected daughter product compounds. Sites featuring a vinyl chloride plume were classified as showing strong evidence of reductive dehalogenation. Those exhibiting a *cis*-1,2-DCE plume, but no vinyl chloride plume, were classified as showing weak evidence of reductive dehalogenation. Those lacking plumes of either of these two compounds were assumed to show no evidence of reductive dehalogenation if other chloroethenes were present. This categorization scheme was found to be consistent with concentrations of chloride ion measured at the sites. Furthermore, concentrations of fuel hydrocarbons (represented by total xylenes) and bicarbonate alkalinity from sites among the three groups suggests the possibility that the oxidation of fuel hydrocarbon co-contaminants may be playing a major role in promoting reductive dehalogenation at the sites in the study.
- Evidence for transformation processes, such as the abiotic transformation of 1,1,1-TCA and reductive dehalogenation, is associated with shorter plume lengths once the effects of source area mass and groundwater velocity are factored out. In the case of reductive dehalogenation, the cumulative distributions of normalized plume lengths indicate that this effect appears to be more pronounced in the 100-ppb-defined plume population than the 10-ppb-defined population. This behavior may be explained by higher transformation rates near the source areas associated with the presence of fuel hydrocarbon compounds. Comparison of the effects of transformation processes on source strength and hydraulic conductivity-normalized plume lengths for CVOCs suggests that reductive dehalogenation rates are relatively slow compared to those of hydrocarbon transformation rates studied previously.
- An inverse correlation was found between mean plume lengths per CVOC (normalized by maximum concentration and hydraulic conductivity) and the associated Henry's constant. This finding is intuitive, given that compounds with higher Henry's constants would exhibit a greater tendency to partition into the gas phase in the vadose zone overlying a phreatic aquifer. This loss of mass out of the aqueous phase could conceivably lead to some shortening of the plume once the effects of other variables are taken into account.
- A correlation was also found between maximum site plume length and the age of the plume as inferred by the elapsed time since the commencement of site operations.
- Monte Carlo simulation using an analytical plume model and inferred probability distributions of hydrogeologic variables was used to generate populations of synthetic plumes. Application of the same analytical approaches to the synthetic plume data as the

field data yielded similar results in terms of scatter in the data and the role of normalization in analyzing plume lengths.

- Among the sites in the study, the level to which a site was characterized, based on the number of monitoring wells versus the overall length of the plume, varied widely. In general, it appears that most sites focus considerable effort collecting data on CVOC concentrations in groundwater, but have under-collected data on hydraulic gradient, hydraulic conductivity, and geochemical indicators. Also, a great deal of variability was observed in plume behavior across the geographic distribution of plumes as well as with reference to the types of sites studied.

CONCLUSION

There is growing evidence that natural processes are degrading contaminants of concern, and that the contribution these natural processes make to achieving cleanup goals needs to be formally considered during site-specific cleanup. The use of historical case data has several advantages, among them: 1) sites can reduce characterization costs by sharing information on key hydrogeologic parameters controlling contaminant fate and transport, and 2) standard reference frameworks can be developed that individual sites can use as a basis of comparison regarding plume behavior.

The appropriate application of natural biodegradation processes as a remediation approach will depend on the anticipated time frame for beneficial use of the affected groundwater. Definition of cleanup times must take into account basic constraints imposed by natural laws governing the transport and natural degradation process of petroleum hydrocarbons. The actual time to reach groundwater cleanup goals is determined by these laws and the limitations on residual subsurface contamination attenuation rates, through either active or natural biological processes. These limitations will practically constrain the time to achieve low concentration cleanup goals.

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REFERENCES

1. Grbic-Galic, D., and T.M. Vogel. 1987. Transformation of Toluene and Benzene by Mixed Methanogenic Cultures. *Applied and Environmental Microbiology*. 53(2): 254-260.
2. Cozzarelli, I.M., M.J. Baedeker, R.P. Eganhouse, and D.F. Goerlitz. 1994. The geochemical evolution of low-molecular-weight organic acids derived from the degradation of petroleum contaminants in groundwater. *Geochemica et Cosmochimica Acta*, 58, 863-877.
3. Hess, A., P. Höhener, D. Hunkeler, and J. Zeyer. 1996. Bioremediation of a diesel fuel contaminated aquifer: Simulation studies in laboratory aquifer columns. *Journal of Contaminant Hydrology*, 23, 329-345.
4. Kazumi, J., M.E. Caldwell, J.M. Suflita, D.R. Lovely, and L.Y. Young. 1997. Anaerobic Degradation of Benzene in Diverse Anoxic Environments. *Environmental Science and Technology*. 31(3): 813-818.
5. Rice, D.W., R.D. Grose, J.C. Michaelson, B.P. Dooher, D.H. MacQueen, S.J. Cullen, W.E. Kastenberg, L.E. Everett, and M.A. Marino. 1995a. *California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses*. Lawrence Livermore National Laboratory, Livermore, California. UCRL-AR-122207.
6. Rice, D. W., B.P. Dooher, S. J. Cullen, L.G. Everett, W.E. Kastenberg, R.D. Grose, and M. Marino. 1995b *Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs)*. Lawrence Livermore National Laboratory, Livermore, California. UCRL-AR-121762.
7. Mace, R.E., C.I. Mayfield, and J.F. Baker. 1997. *Extent, Mass, and Duration of Hydrocarbon Petroleum Storage Tank Sites in Texas*. Bureau of Economic Geology, University of Texas at Austin. Geological Circular 97-1.
8. Chappelle, F.H., P.M. Bradley, D.R. Lovley, and D.A. Vroblesky. 1996. Measuring Rates of Biodegradation in a Contaminated Aquifer Using Field and Laboratory Methods. *Ground Water*. 34(4): 691-698.
9. Borden, R.C., C.A. Gomez, and M.T. Becker. 1995. Geochemical Indicators of Intrinsic Bioremediation. *Ground Water*. 33(2): 180-189.
10. Vroblesky, D.A., and F.H. Chapelle. 1994. Temporal and Spatial Changes of Terminal Electron-Accepting Processes in a Petroleum Hydrocarbon-Contaminated Aquifer and the Significance for Contaminant Biodegradation. *Water Resources Research*. 30(5): 1561-1570.
11. McNab, W.W., Jr. 1997. *Comparisons of Geochemical Signatures of Biotransformation of Fuel Hydrocarbons in Groundwater*, accepted for publication in Environmental Monitoring and Assessment.
12. Buscheck, T.E., and C.M. Alcantar. 1995. *Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation*. In: Proceedings of the 1995 Battelle International Symposium on In Situ and On-Site Bioreclamation.

13. Beckett, G.D., and P. Lundegard. 1997. *Practically impractical – The limits of LNAPL recovery and relationship to risk*, in Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water Prevention, Detection, and Remediation Conference, Houston, Texas, November 12-14.
14. McNab, W.W., Jr., D. W. Rice, J. Bear, R. C. Ragaini, C. Tuckfield, and C. Oldenburg. 1998. *Behavior of Chlorinated Volatile Organic Compound Plumes Based on Historical Case Analysis*. Lawrence Livermore National Laboratory, Livermore, California. UCRL-AR-????.